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AUTHOR(S):

Ashida, Michio; Watanabe, Teizo

CITATION:

Ashida, Michio ...[et al]. Orientation Overgrowth of Polycyclic Aromatic Quinones (Commemoration Issue Dedicated to Professor Eiji Suito on the Occasion of his Retirement). Bulletin of the Institute for Chemical Research, Kyoto University 1975, 53(2): 117-126

ISSUE DATE:

1975-09-25

URL:

<http://hdl.handle.net/2433/76612>

RIGHT:

Orientation Overgrowth of Polycyclic Aromatic Quinones

Michio ASHIDA and Teizo WATANABE

Received March 8, 1975

Polycyclic aromatic quinones (flavanthrone, indanthrone, and pyranthrone) were vacuum-sublimated onto the cleavage faces of muscovite, rock salt, sylvine, and graphite. Films of the quinones vacuum-sublimated on muscovite were composed of triangular networks of long slender crystal strips which took their *b*-axis parallel to the substrate face and ran along with a psuedohexagonal axis of a muscovite crystal. Films on rock salt were composed of needle-like crystallites crossing orthogonally each other, the needle axis of the crystals coincided with the $\langle 110 \rangle$ directions of rock salt. When cleavage faces of muscovite and rock salt were used as the substrate, the planar molecules of the quinones probably stand obliquely on the substrate face so that they come in contact with the interface at several points. Films on sylvine were composed of dendroid crystals which assumed the standing *b*-axis orientation. In this case, the molecular planes come in contact parallelly with the substrate face, giving rise to incline the *b*-axis of the deposited crystal against the substrate face. Crystals condensed on graphite also took a standing *b*-axis orientation and transformed to a new crystal form, which may be caused by a strong attractive force between the deposited molecule and the substrate graphite.

INTRODUCTION

It had been reported that condensed polycyclic aromatic compounds grew epitaxially when they were sublimated onto muscovite *in vacuo*.¹⁾ The evaporated film of phthalocyanine, one of the condensed polycyclic aromatic compounds, were found to take various orientations according to the substrates.^{2,3,4)} The molecules of condensed polycyclic aromatic compounds are composed of large flat planes. In the crystals, the planar molecules are closely packed together in a column and slightly tilted against the column axis. The molecules of polycyclic aromatic quinones, flavanthrone ($C_{28}H_{12}O_2N_2$), indanthrone ($C_{28}H_{14}O_4N_2$), and pyranthrone ($C_{30}H_{14}O_2$), resemble each other in size and shape. The differences in the constituent atoms of these quinones probably cause variation of the interaction between their molecules facing parallel to one another, which gives rise to change of the way of packing their molecules in the crystals. As is described previously,⁵⁾ these quinones vacuum-sublimated on alkali halides took two types of orientations. These two types of orientations were called the parallel *b*-axis and the standing *b*-axis orientation, according to the direction of the *b*-axis of the crystal relative to the substrate face. It was suggested that in the case of organic crystals a single molecule could be regarded as a nucleus and the basic orientation taken by itself determined the orientation of crystal.

In this work, the films of these quinones vacuum-sublimated on various single crystals were examined by electron microscopy as well as by electron diffraction. The resulting

* 芦田道夫, 渡辺禎三 : Department of Industrial Chemistry, Faculty of Engineering, Kobe University, Nada, Kobe.

orientation was discussed in relation to the intermolecular force and the interaction between the deposited molecule and a substrate.

EXPERIMENTAL

The polycyclic aromatic quinones, flavanthrone, indanthrone, and pyranthrone, were purified by repeated sublimation in a low-pressure stream of carbon dioxide at a temperature above 400°C and were examined by means of an X-ray diffractometer. The purified materials in a small quartz crucible were heated by winding tungsten wire and sublimated onto a clean surface of substrate in a vacuum evaporator. Single crystals of muscovite, rock salt, sylvine, and graphite were used as the substrate. They were cleaved in air and immediately placed in the vacuum evaporator. The substrate was kept at a temperature in the range from 100 to 200°C. When muscovite, rock salt, and sylvine were used as the substrate, the deposited films were separated from the substrate by the wet-stripping method after they had been reinforced with evaporated carbon film and prepared for electron microscopy. When a single crystal of graphite was used as the substrate, the deposited film was observed together a very thin sheet of graphite by an electron microscope. Thallium chloride prepared by evaporation *in vacuo* was used as a standard calibration material for the spacing measurement.

RESULTS

When flavanthrone was vacuum-sublimated onto a cleavage face of muscovite at 150°C, the film was built up of triangular networks of slender crystal strips as is shown in Fig. 1(a). Corresponding to such a configuration of the film, the electron diffraction pattern had a hexagonal figure, as Fig. 1(b) shows. The pattern is a superposition of three identical fiber diagrams which cross at an angle of 120° each other. Because the

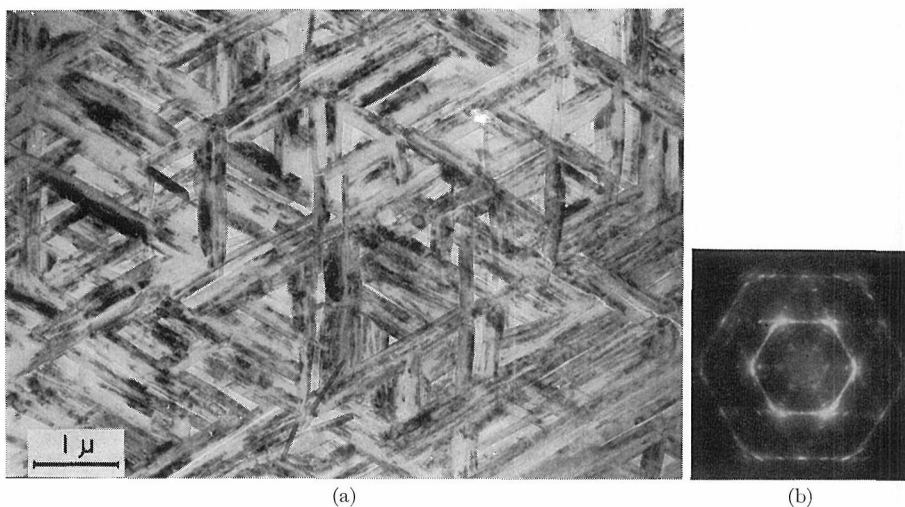


Fig. 1. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-sublimated onto a cleavage face of muscovite.

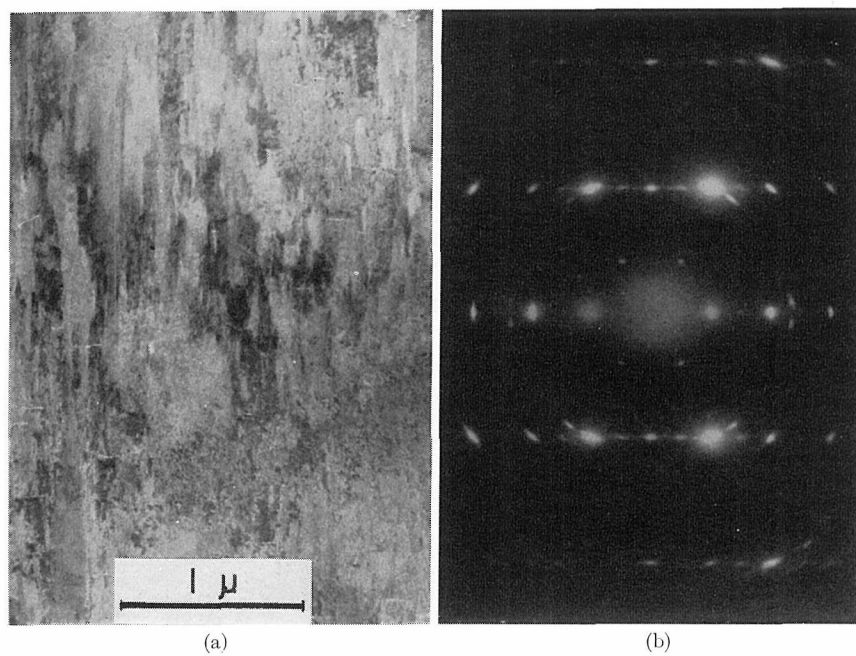


Fig. 2. Electron micrograph (a) and electron diffraction pattern (b) of single crystal film of flavanthrone.

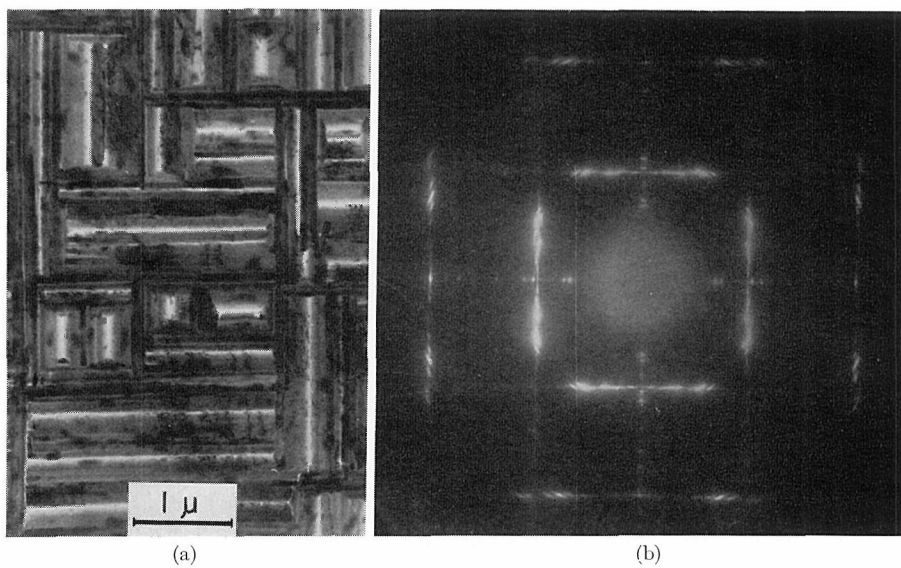


Fig. 3. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-sublimated onto a cleavage face of rock salt.

fiber period obtained from the diffraction pattern showed a good coincidence with the unit length of the b -axis, the b -axis of the crystal strips turned out to be parallel to the longitudinal direction. Two sets of reflection spots simultaneously appeared on the equator, corresponding to the interplanar spacings of the (200) and (001) plane respectively. As has been reported previously,²⁾ the appearance of the two sets of equatorial reflection spots indicates that the film consists of at least two kinds of crystal strips with different lattice orientations. As for the relative orientation of the evaporated film to the substrate, the b -axis of the former was parallel to any one of the three directions which coincided with the a -axis itself and the directions making $\pm 60^\circ$ with the a -axis of muscovite. Sometimes a part of the deposited film was composed of laminar crystal strips with single directional orientation or a nearly single crystal whose electron micrograph and electron diffraction pattern are shown in Figs. 2(a) and (b) respectively. This net pattern shows that the (100) plane is parallel to the face of substrate. However, it was not able to find out the sublimation condition preparing for the single crystal film. The flavanthrone film condensed on rock salt was composed of two groups of slender crystal strips crossing orthogonally each other, as is shown in Fig. 3(a). The diffraction pattern also had an orthogonal appearance, as Fig. 3(b) shows. Each of the crossing fiber diagrams is essentially the same as that observed in the film on muscovite. The needle axis of the slender crystals was found to be parallel to the $[110]$ direction of the rock salt crystal. Consequently, the b -axis of the crystals sublimated on rock salt and muscovite runs parallel to the face of the substrate and grow along the direction depending on the substrate crystal. Many other quinones such as indanthrone, pyranthrone, violanthrone, isoviolanthrone, and anthanthrone assumed the same parallel b -axis orientation, when they were sublimated onto cleavage faces of muscovite and rock salt. The morphology of these condensed films resembled one another. In the electron diffraction patterns, the fiber periods along the meridian were around 3.8 \AA and the two sets of reflection spots generally appeared on the equator. Therefore, it is noted that the electron diffraction patterns from these condensed films closely resemble each other.

On the contrary, when a cleavage face of sylvine was used as the substrate, vacuum-condensed films of flavanthrone showed quite a different orientation from that obtained on rock salt and muscovite. Flavanthrone crystals sublimated on sylvine grew well-defined dendrites and formed a discrete film, as is shown in Fig. 4(a). The electron diffraction pattern of the film shown in Fig. 4(b) appears to overlap two single crystal patterns crossing orthogonally each other in spite of the reflections from many crystallites. This finding suggests that all the crystals deposited on sylvine take a well-defined orientation. The spots on the layer lines above and below the equator correspond to $h14$ (or $h\bar{1}4$) and $\bar{h}14$ (or $\bar{h}\bar{1}4$) respectively. Consequently, the b -axis of the crystal makes an angle of about 28° with the vertical of the substrate face. By relating the orientation of flavanthrone to the substrate crystal, a projection of the former's b -axis on the substrate face was found to coincide with the $[110]$ direction of sylvine. In the case of indanthrone, the deposited film on sylvine was composed of dendroid crystals similar to those of flavanthrone as is shown in Fig. 5(a). The electron diffraction pattern of the film shows a complicated pattern with the C_{4v} symmetry, as is represented in Fig. 5(b). In the previous paper,⁴⁾ the diffraction spots were indexed as is shown in schematically in Fig. 6, in which the white circles indicate the basic single crystal pattern associated with one of

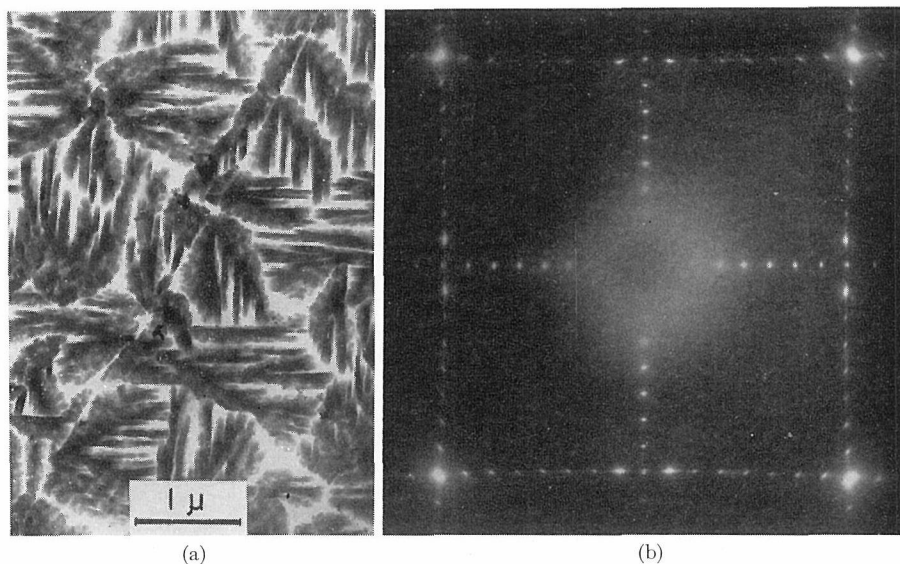


Fig. 4. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-sublimated onto a cleavage face of sylvine.

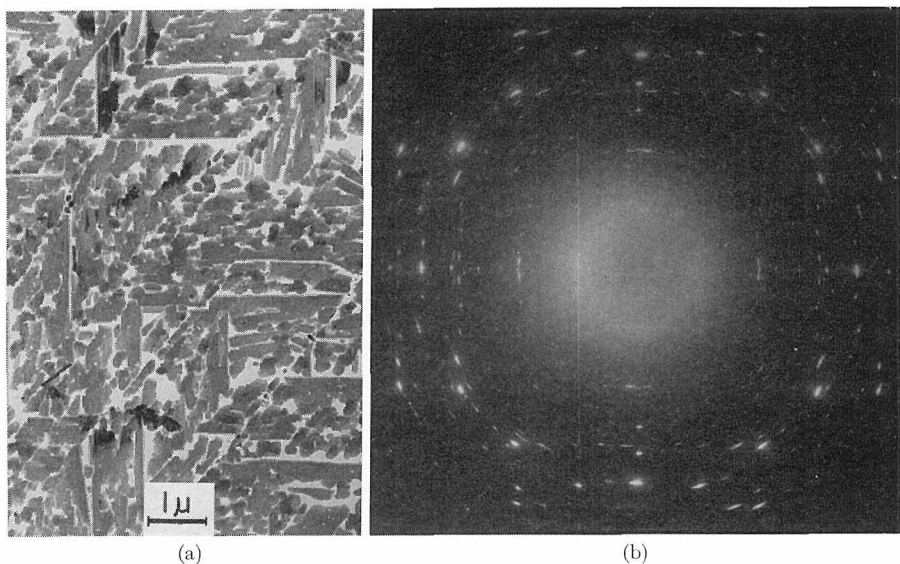


Fig. 5. Electron micrograph (a) and electron diffraction pattern (b) of indanthrone film vacuum-sublimated onto a cleavage face of sylvine.

two groups of crystals which have an apparent C_2 symmetry. The total pattern was illustrated by the systematic superposition of this elementary pattern with the major axes of C_{4v} symmetry, XX' and YY' , which further coincided with the $[110]$ and $[\bar{1}\bar{1}0]$ directions of sylvine respectively. Consequently, the a -, b -, and c -axes of the crystal are inclined to the vertical of the substrate face at angles of about 120° , 35° , and 76° respectively. Each reciprocal c^* axis was found to make an angle of about 5° with the nearest major axis of C_{4v} symmetry. On the other hand, the film of pyranthrone sub-

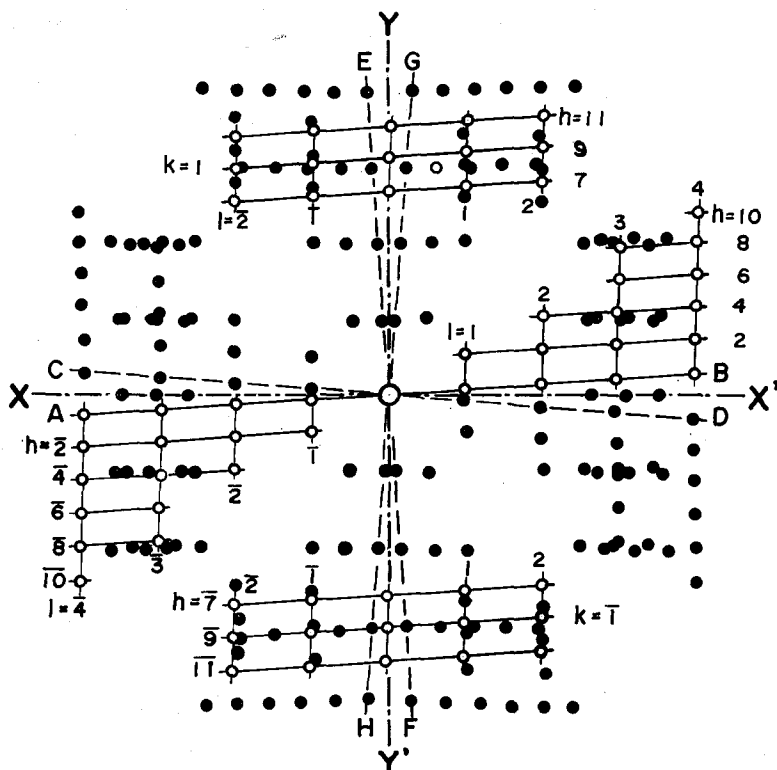


Fig. 6. The interpretation of the diffraction pattern shown in Fig. 5(b). White circles are the representation of the basic single crystal pattern.

limited on sylvine showed the reflection pattern of imperfect ring diagram. The finding random orientation arises from the differences in the tilting directions of the b -axis of the individual crystallites, though the inclination angle of each b -axis to the vertical of the substrate face is always a constant value of 29° .

Because the film vacuum-sublimated on graphite stuck fast to the substrate, it could not be detached from the later. The deposited film was observed by an electron microscope as it sticks on graphite. The deposited film was composed of small flaky crystals as is shown in Fig. 7(a). The electron diffraction pattern of Fig. 7(b) shows the superposition of the reflection spots from the deposited crystals of flavanthrone and those from the substrate graphite. Many satellites by a double-diffraction effect are observed around the reflection spots from graphite which indicate with arrows in the figure. In this case, the crystal axes of deposited film inclined to the substrate face and the deposited crystal took a different crystal form from the stable form reported previously.⁶⁾ In order to obtain the crystal data for this modification, the unit cell dimensions were determined by means of electron diffraction method. When the film is tilted against the incident beam so that a crystal axis becomes parallel to the beam, the intensity distribution symmetrized with respect to the origin. As the incident beam is parallel to the crystal b -axis, the diagram shows the reciprocal lattice points with the $h0l$ indices. Furthermore, by rotation of the film against the incident beam, another crystal axis becomes parallel to the

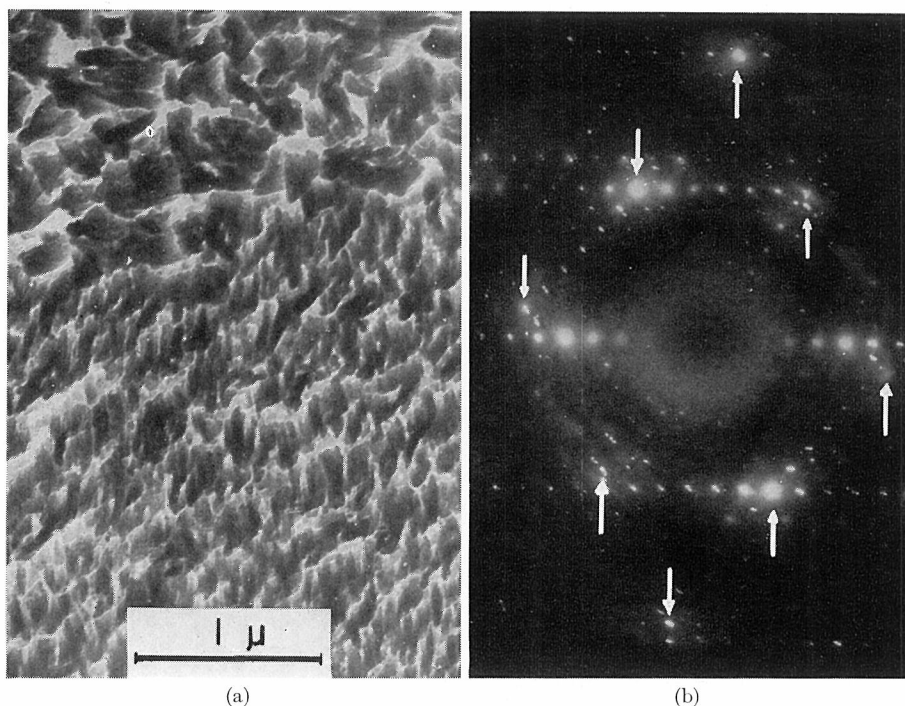


Fig. 7. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-sublimated onto a cleavage face of graphite.

beam and the diffraction pattern shows the net diagram from a basal plane. The lattice constants of the unit cell were determined from the net pattern obtained by this method, as is shown in Table I. When the film inclines against the incident beam, the Ewald sphere crosses the elongation in the intensity region of the reciprocal lattice points caused by very thin sheet of graphite and the hexagonal spots on a circumference transform into those on an ellipse. Consequently, the inclination angles of the crystal axes to the substrate face were obtained from the deformation of hexagonal reflection spots from graphite. The crystal data for other quinones condensed on graphite and the inclination angles of these crystals to the substrate were also obtained by the same method, as is shown in Table I. The results will be described in detail in other report.

Table I. Crystal Data of Quinone Crystals Vacuum-Sublimated on Graphite

		Flavanthrone	Indanthrone	Pyranthrone
Cell dimensions	a (Å)	27.5	28.6	21.3
	b (Å)	3.48	3.83	3.47
	c (Å)	10.4	8.03	21.5
	α	90°	83°	90°
	β	108°	92°	97°
	γ	90°	90°	90°
Angle between the b -axis and the normal of molecular plane		16°	36°	20°

DISCUSSION

The crystal data of flavanthrone,⁶⁾ indanthrone,⁷⁾ and pyranthrone⁸⁾ reported previously are summarized in Table II. The molecules of polycyclic aromatic quinones are composed of many condensed benzene rings and form a flat plane, or a nearly flat one, as a whole. These flat molecules are closely packed together in a column, giving rise to a tilt against the column axis. The inclination angles of the molecular plane against the each crystal axis are shown in Table II. When the quinones were sublimated onto muscovite, either the (001) or (100) plane of the deposited crystal lay parallel to the substrate surface and the individual slender crystal strips grew along any one of three directions which coincided with the pseudohexagonal axis in the cleavage face of muscovite. Thus, the film was composed of triangular networks of slender crystals as a whole. The direction of this pseudohexagonal axis corresponds to a row of K^+ ions in the cleavage face of muscovite. Similarly, the film sublimated on rock salt was composed of slender needle-like crystals with the same two crystal habits as those on muscovite and its b -axis ran along the $\langle 110 \rangle$ directions of rock salt which coincided with a row of Na^+ ions. The polycyclic aromatic quinones are apt to crystallized in slender needle-like lamellae. Therefore, the outward appearances of individual crystals in the films are mainly ascribed to the natural properties of such compounds themselves. The needle-like crystals grow along the like-charged ions on the surface of substrate. Since the planar molecules tilt against the (001) and (100) planes, they stand obliquely on the substrate face so that they come in contact with the interface at several points.

On the contrary, when sylvine was used as the substrate the deposited films showed quite a different orientation, giving rise to a distinct morphorogy. In the case of flavanthrone crystal on sylvine, its b -axis is inclined to the vertical of the substrate face at an angle of 28° and the a -axis run along the $\langle 110 \rangle$ directions of sylvine. Because the molecular plane of flavanthrone is inclined against the (010) plane at an angle of 26° , the standing b -axis orientation suggests that the planar molecule nearly comes in contact parallelly with the substrate face. As is described previously⁵⁾ the nitrogen atoms of the molecule probably come in contact with K^+ ions, as schematically shown in Fig. 8. A projection of the above molecule facing parallel along the b -axis on the molecular plane

Table II. Crystal Data of Quinones

		Flavanthrone	Indanthrone	Pyranthrone
Unit cell constants	a (Å)	27.9	30.8	22.0
	b (Å)	3.80	3.83	3.84
	c (Å)	8.10	7.84	21.2
	β	95°	92°	90°
	z	2	2	2
Space group		$P2_1/a$	$P2_1/a$	$P2_1/n$
Angles between crystal axes and the normal of molecular plane				
	a -axis	$105^\circ, 73^\circ$	$110^\circ, 80^\circ$	
	b -axis	26°	26°	26°
	c -axis	$72^\circ, 108^\circ$	$75^\circ, 105^\circ$	

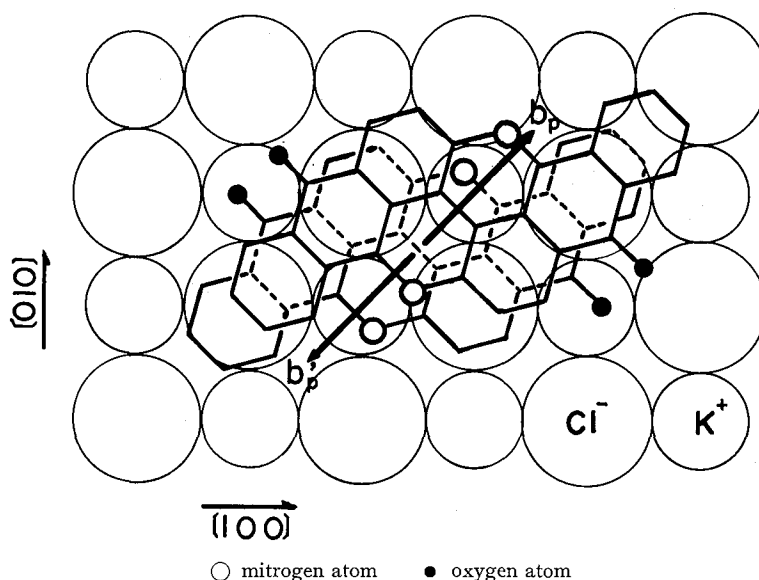


Fig. 8. Schematic diagram of the relative orientation of flavanthrone to the (001) plane of KCl.

shifts in either the b_p or b_p' direction, which coincides with the $[110]$ direction of sylvine, depending upon the staggering of the overlapping molecule. This configuration results in two different crystals which are related by a two-fold rotation axis. According to the symmetry of sylvine, the total film consists of four groups of oriented crystals and the electron diffraction pattern from them gives two overlapping diagrams crossing orthogonally. The crystals of indanthrone sublimated on sylvine also took the standing b -axis orientation, in which the a -, b -, and c -axes are inclined to the vertical of the substrate face at angles of about 120° , 35° , and 76° respectively. In the pyranthrone film vacuum-sublimated on sylvine, the individual crystal assumed the standing b -axis orientation, in which the b -axis tilted against the substrate face with an angle of 29° . Consequently, it is clear that the flat molecules of indanthrone and pyranthrone lie nearly parallel to the substrate face when they are condensed on sylvine. On the basis of this finding, it is reasonable to postulate that a nucleus is built up by a planar molecule coming in contact parallelly with the cleavage face of sylvine and then deposited molecules arrange around the nucleus in the inherent way of packing so that the crystal grow in the direction of the b -axis. Therefore, the deposited crystal assumes the standing b -axis orientation in which the b -axis takes the characteristic angle against the substrate face. The electron diffraction pattern of the film also shows the characteristic diagram corresponding to the tilting angle of the crystal. The competition between the adsorption force of the deposited molecule on the substrate face and the intermolecular force in the crystal probably leads the discrepancy between the inclination angle of the molecular plane and the tilting angle of the b -axis.

The crystals of quinones vacuum-condensed on graphite also assumed the standing b -axis orientation. As a result of strong attractive force between the deposited molecules and substrate graphite, the crystals deposited on graphite transform to the new

form whose crystal data are given in Table I. In the new form of flavanthrone and pyranthrone, the unit length of the individual b-axis, which corresponds to the distance between parallel molecular plane along this axis, decreases from 3.8 Å for the stable form to 3.48 Å. The latter value comes near to 3.35 Å, the layer distance of graphite itself. Moreover, the *b*-axes of flavanthrone and pyranthrone incline to the vertical of the substrate face at angles of 16° and 20° respectively, which are smaller than the inclination angle of the b-axis in each stable form. This finding suggests that these molecular planes increase the tilting angle against the *b*-axis and are packed more closely. Consequently, it seems that the quinone molecule adsorbs on graphite so strongly that it may be regarded as a segment of graphite, and arrange in graphite-like structure, giving rise to form a new crystal type. The deformation of the crystal is determined presumably by the interaction between the intermolecular force and attractive force of graphite.

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